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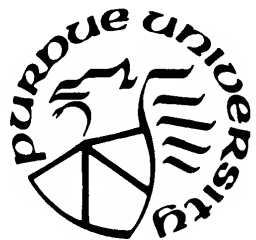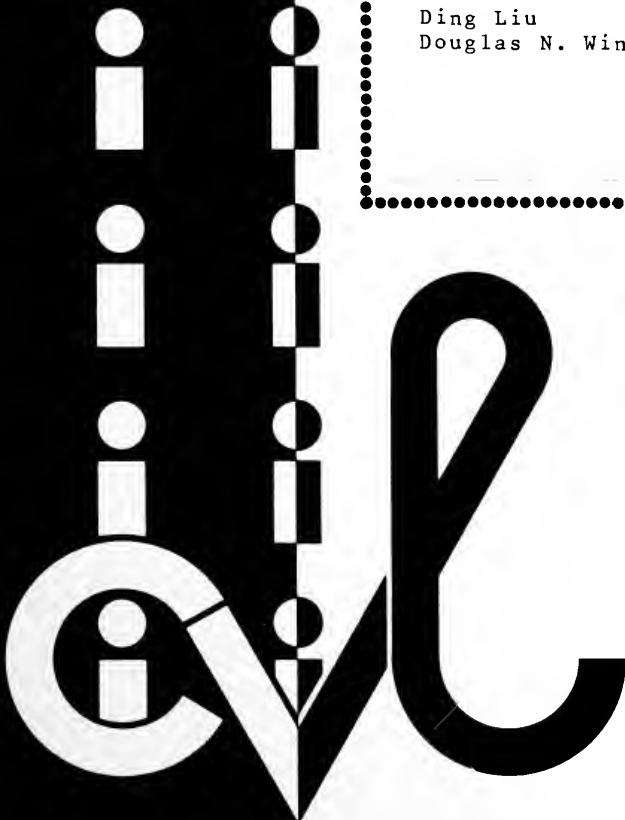
INDIANA
DEPARTMENT OF HIGHWAYS

JOINT HIGHWAY RESEARCH PROJECT

FHWA/IN/JHRP-86/13

Final Report

THE PORE STRUCTURE OF CONCRETE

Ding Liu
Douglas N. Winslow

PURDUE UNIVERSITY

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To: H.L. Michael   August 27, 1986
        Joint Highway Research Project
                                             Project: C-36-57B
From: D.N. Winslow
        Joint Highway Research Project File: 5-12-2

    The Final Report attached is submitted on the HRP Part II Research Study titled "The Pore Structure of Concrete". Mr. Ding Liu has performed the research and authored the report under my supervision.

    The objective of the study was to measure the pore structure of hydrated cement paste as it forms in the presence of aggregate in concrete. Recent studies have indicated that this pore structure might be different from that present in plain cement paste. The pore structure of the paste in concrete was measured by making samples with non-porous aggregate, and by correcting for the mass of aggregate that was present in the sample. The results show that the pore structure of paste in concrete is different in important ways from the that found in plain pastes.

    The report is submitted for presentation to the JHRP Board, and for review by DOH and FHWA.

                                    Respectfully submitted,

                                    D.N. Winslow
                                    Research Associate

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16. Abstract

The pore size distributions of cement pastes and the pastes in concrete and mortar hydrated under different conditions were measured by mercury intrusion. The measurements were made at the same degrees of hydration for all the samples. In order to measure the pore size distribution of the paste in concrete and mortar, a non-porous quartzite aggregate was used and an EDTA titration method was used to determine the paste content of the concrete and mortar.

A difference was found between the pore size distributions of the plain paste and the paste in concrete and mortar. The distributions in concrete and mortar were essentially the same. The paste that forms in concrete was found to be more porous than plain paste. Further, this difference was greater for older samples with a greater degree of hydration. The majority of the extra porosity has pore diameters that are about ten times as large as the largest ones in plain paste. This was found to be true for pastes with different water:cement ratios, pastes hydrated at different temperatures, and pastes with accelerators and retarders.

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Final Report

THE PORE STRUCTURE OF CONCRETE

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Federal Highway Administration

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HIGHLIGHT SUMMARY

The Pore size distributions of cement pastes and the pastes in concrete and mortar hydrated under different conditions were measured by mercury intrusion. The measurements were made at the same degrees of hydration for all the samples. In order to measure the pore size distribution of the paste in concrete and mortar, a non-porous quartzite aggregate was used and an EDTA titration method was used to determine the paste content of the concrete and mortar.

A difference was found between the pore size distributions of the plain paste and the paste in concrete and mortar. The distributions in concrete and mortar were essentially the same. The paste that forms in concrete was found to be more porous than plain paste. Further, this difference was greater for older samples with a greater degree of hydration. The majority of the extra porosity has pore diameters that lie in a range between the largest pores present in plain paste and diameters that are about ten times as large as the largest ones in plain paste. This was found to be true for pastes with different water:cement ratios, pastes hydrated at different temperatures, and pastes with accelerators and retarders.

INTRODUCTION

Portland cement concrete is a particulate composite material in which aggregate is the dispersed phase and cement paste is the continuous phase. The properties of the cement paste critically affect the performance of the concrete, and understanding the microstructure of cement paste is a crucial part of concrete research. Much work has been done to investigate the microstructure of cement paste, and a large body of knowledge about this material has been obtained. This knowledge plays an important role in understanding and improving the performance of concrete.

It has been conventional to assume that the paste phase in mortar and concrete has the same microstructure as it has when cement and water react to form paste in the absence of aggregate. Hence, it has been assumed that what is known about plain hardened cement paste is applicable when the paste acts as the cementing matrix in mortar or concrete. However, some recent findings have indicated that the paste near the aggregate-paste interface is different from that in the bulk volume of paste, and have called into question the above assumption.

Hadley [1] investigated the paste-aggregate interface with scanning electron microscopy. Based on this work, he was able to present a picture of the development of the microstructure at the paste-aggregate interface. He found a considerable volume of water-filled void space remaining at the paste-aggregate interface after consolidation of the paste. At later ages, a characteristic structure with several distinct features develops, in a definite sequence, at this interface. This structure is composed of an oriented layer of $Ca(OH)_2$ on the surface of the aggregate, a subsequent layer of hydrated calcium silicate gel and then large $Ca(OH)_2$ crystals connecting the aggregate and the bulk volume of paste. In this picture the total influenced distance from the aggregate surface may be about 30 μm.

Based on Hadley's work, Barnes [2] made further investigations of the structure of the paste-aggregate interface using the same method. His work verified Hadley's results, and added more details to the picture of the structure of the interface. One of his conclusions was that a layer of secondary $Ca(OH)_2$ is deposited in available space between the layer structures and the overlying paste. He also confirmed that bond cracks do occur near the paste-aggregate interface even in specimens that have never been loaded.

Grandet and Ollivier [3] investigated the growth of $Ca(OH)_2$ crystals near the paste-aggregate interface. They found that the degree of orientation of $Ca(OH)_2$ crystals

varies with the distance from the interface. The orientation limit, which refers to the the distance within which orientation of $Ca(HO)_2$ is detected, varies with water:cement ratio. Typical values lie in the range 20 to 50 μm for pastes with water:cement ratios between 0.25 and 0.33. This indicates that the presence of the paste-aggregate interface affects the structure of the nearby cement paste to a considerable degree.

In studying crack propagation in concrete, Diamond et al [4] measured the distances between aggregate particles on polished cut surfaces of several concretes. They found that this distance is surprisingly small. The mean value measured was 100 μm for a rich concrete and 75 μm for concrete of high sand content. They concluded that because aggregates in concrete are so close together most of the paste is under the influence of the aggregate-paste interface, and different in some ways from bulk paste prepared by itself.

Winslow [5] pointed out that the pore structure of the paste phase in mortar and concrete may be different from that of plain paste. He investigated the pore structure of mortar with the mercury intrusion method and found that the pore structure of the paste in a mortar is different from that of a pure paste. The former has less pore volume in the diameter range of 0.1 - 1 μm and greater pore volume in the diameter ranges smaller than 0.1 μm and bigger than 1 μm.

The porosity of concrete occurs in both the paste and aggregate components. A pore size distribution will reflect the porosity of both phases. To investigate the pore structure of only the paste phase, the porosity due to the aggregate must be eliminated by using a non-porous material. The pore volume of a sample of concrete will vary from sample to sample, even when a non-porous aggregate is used, because of varying paste contents. Thus, the pore volume must be expressed on a basis of unit mass of paste if comparisons are to be made among test results.

The present research has been done to extend Winslow's work to the pore structure of the paste phase in both mortar and concrete. A non-porous, quartzite aggregate was used to eliminate the pore volume of the aggregate. A chemical analysis procedure was used to determine the paste content of the individual mortar and concrete samples whose pore structures had been measured. This made it possible to compare the pore structure of the paste phase in mortar and concrete with that of plain pastes.

EXPERIMENTAL WORK

The plan of this research was to measure the pore structure of a series of concrete samples each of which differed from the others in some controlled way, such as water:cement ratio, curing temperature, etc. In each case, companion samples of mortar and plain paste were also prepared. After appropriate hydration periods, the pore structures of the samples were determined by mercury intrusion. All samples were tested at two different degrees of hydration: approximately 9.5% and 14.5% non-evaporable water content. After intrusion, the paste content of each sample was determined chemically.

Materials

The samples in this work were either pastes, mortars or concretes. The portland cement was the same for all. It was an ASTM Type I (lab number 325) cement. Its composition and some properties are listed in Table 1.

The aggregate was a non-porous quartzite from Baraboo, Wisconsin. It was used to eliminate the effect of the pore volume of the aggregate on the pore structure measurement. The rock was crushed and sieved into both fine and coarse aggregate size fractions. The gradation of the aggregate

Table 1 Composition and Properties of #325 Cement

Composition, %		Properties	
SiO_2	21.12	Setting Time, min.	
Al_2O_3	5.40	Initial	80
Fe_2O_3	2.27	Final	170
CaO	65.24		
MgO	1.22	Fineness	
SO_3	2.97	Wagner, cm^2/g	1750
Na_2O		Blaine, cm^2/g	3335
K_2O	0.78		
Mineral Composition, %			
C_3S	57.02		
C_2S	17.62		
C_3A	10.47		
C_4AF	6.90		

used in the mortar and most of the concrete was selected according to ASTM C-33. The maximum size of aggregate in the concrete was 2.5 cm, and that for the mortar was 4.75 mm. The minimum size of aggregate used was that passing the #50 sieve and retained on the #100 sieve for both mortar and concrete. The gradations of the aggregate are listed in Table 2.

The concrete mix was proportioned using the procedure recommended by ACI Committee 221.1 [6]. The amount of the aggregate in the mortar was chosen such that the total sur-

Table 2   Gradations of Aggregate

Sieve Size	Concrete, % Passing	Mortar, % Passing
1"	100.0	
3/4"	96.4	
1/2"	81.4	
3/8"	60.4	
#4	39.7	100.0
#8	37.6	94.4
#16	25.4	64.6
#30	16.0	41.4
#50	7.5	19.0
#100	0.0	0.0

face area of the aggregate per unit weight of paste was the same for concrete and mortar. This was achieved by using the same fine aggregate in the mortar as that used in the concrete but in larger amount.

The mixing water was deionized. The admixtures, $CaCl_2 \cdot 2H_2O$ and citric acid, were analytical grade. A water reducer, Pozzolith-R, manufactured by Master Builders, Inc. was also used in one mix.

Preparation of Samples

Eight groups of samples were prepared. Groups 1 through 6 consisted of paste, mortar and concrete specimens. The 7th and 8th groups consisted only of two kinds of concrete specimens; they were two concrete mixes widely used in Indiana highway construction [7]. The variables that distinguished each group are given below.

Group 1: w/c=0.45, hydrated at 20°C

Group 2: w/c=0.55, hydrated at 20°C

Group 3: w/c=0.45, hydrated at 10°C

Group 4: w/c=0.45, hydrated at 30°C

Group 5: w/c=0.45 with 2% CaCl$_2$.H$_2$O, hydrated at 20°C

Group 6: w/c=0.45 with 0.15% citric acid, hydrated at 20°C

Group 7: Indiana DOH Class A concrete, hydrated at 20°C

Group 8: Indiana DOH Class C concrete, hydrated at 20°C

All mixing was done in a stainless steel mixing chamber. It was of a cylindrical form with a removable lid, and a valve on the side. A rubber O-ring sealed the removable lid. The weighed amounts of cement and aggregate were put into the mixing chamber, the chamber was connected to a vacuum pump and evacuated for 15 minutes. After evacuation, the required amount of deionized water was introduced into the chamber through the valve on the side without admitting any air. Then the chamber was put on a Red Devil paint shaker to mix for 2 minutes. When admixtures were used, they were dissolved in the mix water in the appropriate amounts. The mix proportions of the samples are listed in Table 3.

For several mixes, made early in the study, the cement and aggregate were dry mixed for 3 minutes, then water was added, and they were mixed for 10 more minutes. It was found that this mixing process had a strong grinding effect on the cement. So, the mixing time was reduced to 2 minutes

Table 3 Mix Proportions

Group #	Water,ml	Cement,g	Aggregate,g
Concrete,w/c=0.45	164	364	1491
Concrete,w/c=0.55	200	364	1491
Mortar, w/c=0.45	52	116	212
Mortar, w/c=0.55	64	116	212
Concrete A	125	260	1411
Concrete C	112	273	1347

of wet mixing only.

After mixing, the vacuum in the chamber was released and the chamber was opened. For concrete, the samples were cast in 3x6 inch cylindrical molds. One third of the mold was filled, and the mold was put on a vibrating table to vibrate until no air bubbles came out. Then the second third of the mold was filled and vibrated in the same way, and so on. After casting, the mold was sealed in a plastic bag. The mortar samples were cast in plastic test tubes with a 1 inch inside diameter and about 3 to 4 inches long, in the same way as the concrete samples. The paste samples were cast in the same plastic tube as used for the mortar samples, but generally without vibration, because the paste had a high flowability. After casting, the plastic tubes were sealed with rubber stoppers.

Generally, the samples were demolded after one day and put into lime-saturated water until the test date. All samples were stored at room temperature, $20^{\circ}C$, except the two

groups that were stored at 10°C and 30°C.

At the desired age, the sample was taken out of the lime water, and several small pieces were cut from it. Since breaking with a hammer may cause many cracks, all the samples used in the study were prepared by sawing. The concrete samples were cut with a Supermatic-300 diamond saw, manufactured by Clipper Manufacturing Company, and the mortar and paste samples were cut with a small Iosmet, low speed saw, manufactured by Buehler LTD.

The size of the sample was chosen such that the intrusion volume of the sample would lie in the range of the porosimeter, and be as large as possible. The samples were about 4 grams for concrete, 1.5 grams for mortar, and 0.8 grams for paste. After cutting, the samples were dried and stored in a vacuum oven at 110°C to prevent carbonation until the time of testing.

Determination of Non-evaporable Water

The non-evaporable water content was determined as the weight loss of the sample on ignition in a muffle furnace at 1050°C. The ignition time was 30 minutes, and platinum crucibles were used. Three duplicates were tested for every sample, and the average value was used as the final result. The sample size used was about 1.5 g for paste, 2 g for mortar and 9 g for concrete. The losses on ignition of the cement and aggregate were also measured, in order to make

the necessary corrections to the final results.

Determination of Total Porosity

The total porosity of the samples was determined by measuring their evaporable water content. When the sample was taken out of lime water, the sample was wiped with a piece of tissue and weighed. It was then put into the vacuum oven to dry for at least one day. The weight of the dry sample was then measured, and the difference between the saturated surface dry weight and the dry weight was taken as the weight of evaporable water. The volume of this water was taken as the total pore volume of the paste fraction.

Mercury Intrusion

The pore size distributions of the samples were obtained by mercury intrusion. The instrument used was a 60,000 psi porosimeter, manufactured by American Instrument Company. With this machine, the minimum intruding pressure was about 20 mm Hg and the maximum was 60,000 psi. These correspond to a measurable range of pore diameters between about 320 μm and 20 A. The intruded volume could be read to an accuracy of ± 0.001 cm^3. The details of the corrections to the raw data were described in [9].

To calculate the pore diameters, a value for the contact angle must be chosen. A wide range of values has been used, from 116° to 140°, for cement paste. A change in the

contact angle from 116° to 140°, at a pressure of 800 psi, will change the corresponding diameter from 0.15 μm to 0.26 μm, and at a pressure of 60,000 psi, the smallest diameter intruded will change from 20 A to 35 A. Shi and Winslow [10] found that appropriate contact angles were: 129° for 1 day old cement paste and 123° for 1 month old cement paste. Winslow and Diamond [9] found that the contact angle was 130° for a P-dried paste, and 116° for an oven dried paste that was 9 months old. These results indicate that, for cement pastes with different ages, the contact angle may be different. The value of contact angle assumed in this study was 116°, obtained by Winslow and Diamond for the oven dried sample.

Determination of Paste Content of Mortar and Concrete

The paste content of each mortar and concrete sample was determined from the weight of cement in the sample and a separate determination of the non-evaporable water of the paste. The amount of cement in the sample was determined by EDTA titration of calcium. The sample, after either igni-tion or mercury intrusion, was dissolved in dilute HCl, and the solution was separated from insoluble material, most of which was aggregate, by filtration. Then the solution was titrated with EDTA to determine the amount of CaO, and the cement content of the sample was calculated from the amount of CaO in the cement. Since the quartz aggregate was inso-luble in HCl, it did not affect the determination of CaO.

The detailed procedure for the determination of the cement content is given in Appendix I.

Intruded samples retained some mercury and so could not be ignited. Therefore, the non-evaporable water content of an intruded sample was assumed to be the same as that determined by ignition of companion specimens that had not been intruded. These were found to give highly reproducable results.

Determination of Air Content

To investigate the effect of air bubbles on the pore volume of the paste in concrete, the air content of the concretes with water:cement ratios 0.45 and 0.55 was determined with an optical microscope. A slice was cut from the sample cylinder and was ground successively with #100, #240, #800, and #1200 grits. Then a square with a side of 5 cm was chosen on the polished surface of the slice. The diameter of every section of an air bubble in the square was measured with a microscope at a magnification of 100X. The smallest diameters observed were 70 to 100 μm. The accuracy of the measurement was ±30 μm. The air content was obtained by dividing the total area of air bubbles on the surface by the area of the square. Usually, the air content of a concrete is measured with a point count method. This method is theoretically the same as that used in this work. Because the air content of the samples was small, an area determina-

tion was believed to be more accurate.

Correction of Entrapped Air Content for Mercury
Intrusion Results

In this paper the pore size distribution curves are presented after the volume of the entrapped air contents are subtracted. The correction for the entrapped air content was made in the following way. All of the distributions displayed a pore diameter where significant intrusion began to occur. At larger diameters there was only modest intrusion, and at slightly smaller diameters there was a large amount of intrusion. The diameter that divides these two regions in the distributions is called the threshold diameter. For pore volumes with diameters far smaller than the threshold diameter, the total measured air content was subtracted from the intruded volumes. Near the threshold diameter, because some air bubbles cannot be reached during the intrusion, some uncertainty exists in the correction of air content. In this paper, the correction is made by subtracting gradually smaller volumes from the cumulative intruded volume, as the threshold diameter is approached, and the correcting values were chosen so that the smooth form of the pore size distribution curves was retained.

RESULTS

Measurement of Porosity

The total porosity of the samples was measured for all 8 groups of samples, including paste, mortar and concrete. The results are listed in the Tables 4, 5, and 6, for the concrete, mortar and paste, respectively. The results are presented as the pore volume per gram of oven dried paste. Other values such as age, total mercury intrusion volume, and non-evaporable water content (Wn/C) are also summarized in these tables.

Table 4   Summary of Results for Concrete

Group No.	Age	Wn/C %	Total Pore Vol. cm^3/g	Pore Vol. Intru. cm^3/g
1	21hr.	9.77	0.3572	0.307
1	20d	14.80	0.3179	0.244
2	27hr.	9.04	0.4144	0.339
2	14d	14.11	0.3932	0.287
3	2.5d	9.53	0.3528	0.286
3	25d	14.45	0.3282	0.249
4	15hr.	9.75	0.3476	0.310
4	8d	14.23	0.3003	0.205
5	11hr.	9.42	0.3633	0.318
5	6d	14.06	0.3363	0.230
6	2d	9.45	0.3489	0.306
6	16d	14.48	0.2975	0.213
7	30hr.	9.59	0.3552	0.297
7	11d	14.11	0.3374	0.250
8	29hr.	9.97	0.2935	0.246
8	21d	14.19	0.2735	0.199

Table 5   Summary of Results for Mortar

Group No.	Age	Wn/C %	Total Pore Vol. cm^3/g	Pore Vol. Intru. cm^3/g
1	22hr.	9.11	0.3422	0.285
1	20d	14.80	0.3082	0.228
2	26hr.	9.30	0.4111	0.348
2	11d	14.52	0.4013	0.295
3	5d	9.76	0.3428	0.264
3	25d	13.91	0.3076	0.219
4	15hr.	9.86	0.3395	0.270
4	10d	14.67	0.3025	0.198
5	11hr.	9.60	0.3490	0.299
5	6.5d	14.71	0.3287	0.213
6	5d	9.56	0.3492	0.269
6	17d	14.24	0.3243	0.225

Table 6   Summary of Results for Paste

Group No.	Age	Wn/C %	Total Pore Vol. cm^3/g	Pore Vol. Intru. cm^3/g
1	1.5d	9.97	0.3466	0.277
1	21d	14.81	0.3026	0.190
2	27hr.	9.26	0.4410	0.353
2	21d	14.82	0.3615	0.241
3	5d	9.30	0.3623	0.275
3	42d	14.40	0.3144	0.185
4	26hr.	9.42	0.3551	0.273
4	14d	14.62	0.3125	0.198
5	24hr.	9.56	0.3637	0.285
5	7d	14.92	0.3288	0.215
6	7d	9.33	0.3728	0.274
6	50d	14.22	0.3263	0.196

The pore volume values listed are the averages of three duplicates. In the case of plain pastes, the range of duplicate values was small. However, for mortars and concretes, especially concretes, the range was larger, up to

0.01 cm^3/g. This difference may be due to the existence of air bubbles and cracks in the samples.

Measurement of Air Content

The air contents of concretes with water cement ratios of 0.45 and 0.55. were measured and the results are presented in Table 7.

Table 7   Results of Air Content Measurement

Concrete	Air Content, cm^3/g
W/C=0.45	0.021
W/C=0.55	0.005

In the table, the results have been presented in terms of pore volume per gram of paste in the concrete.

Measurement of Pore Size Distribution

The pore size distributions of the pastes and the pastes in concretes of all 8 groups of samples were measured. The results are presented as the pore volume per gram of oven-dry paste. The later value was obtained by dividing the intrusion volume by the weight of paste in the sample. All the measurements were carried out at as close as possible to two values of degree of hydration. For every sample two duplicates were tested and, generally, the average of the two results was taken as the final result. In several cases, an apparent error occurred in one of the tests, and

that result was discarded. All the results, corrected for air content are plotted in Fig.1 to Fig.16. The pore size distributions of the pastes in mortars were nearly the same as those in corresponding concretes. Hence, they are presented only for the groups of samples with water:cement ratios 0.45 and 0.55. In other cases, only the plain paste and concrete results are presented.
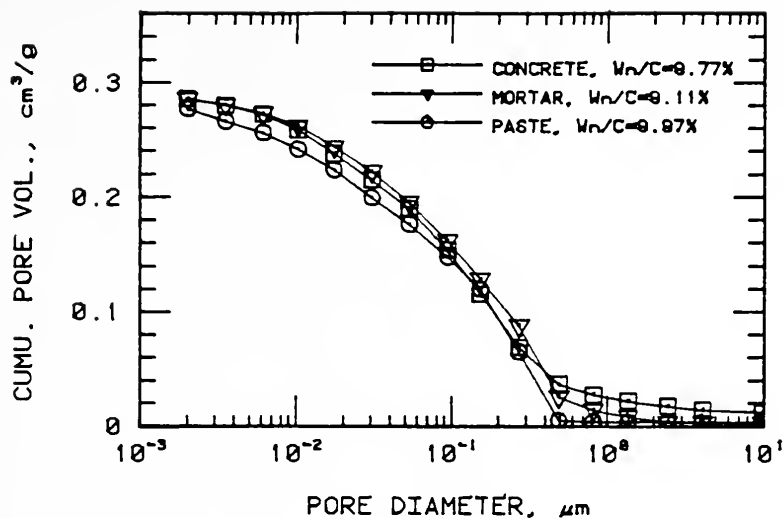
Fig.1 The pore size distributions of the paste and the
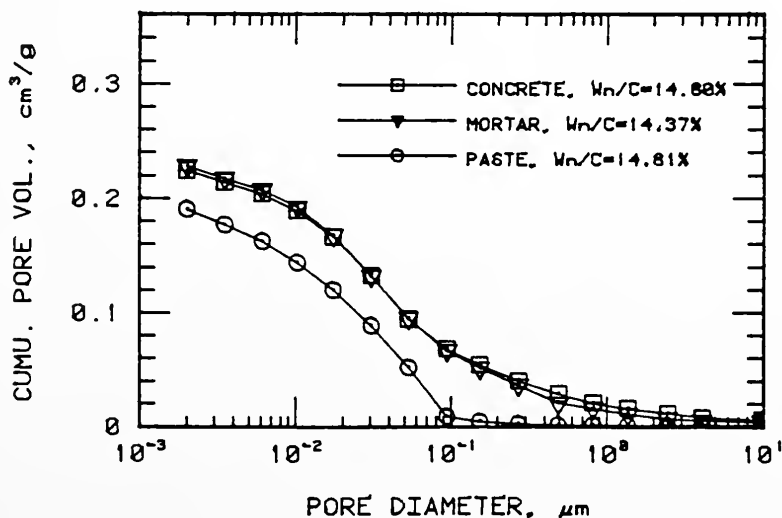paste in concrete and mortar with w/c=0.45 at an early age.

Fig.2 The pore size distributions of the paste and the paste
in concrete and mortar with w/c=0.45 at a later age.

Fig.3 The pore size distributions of the paste and the
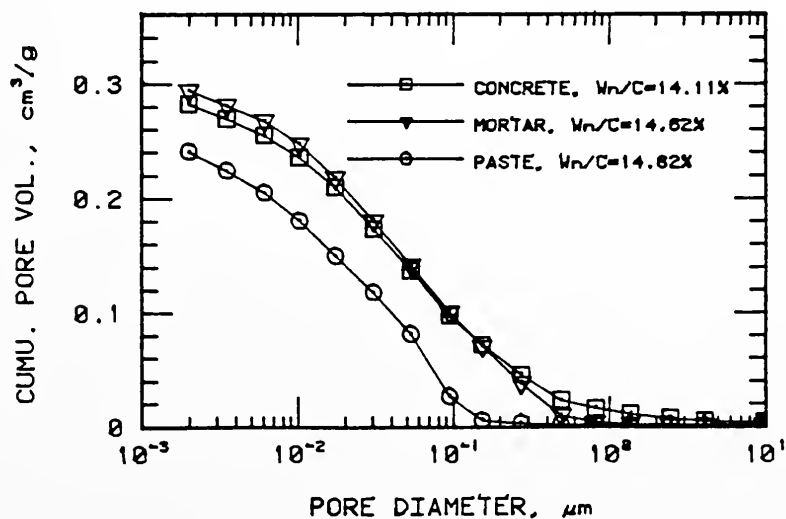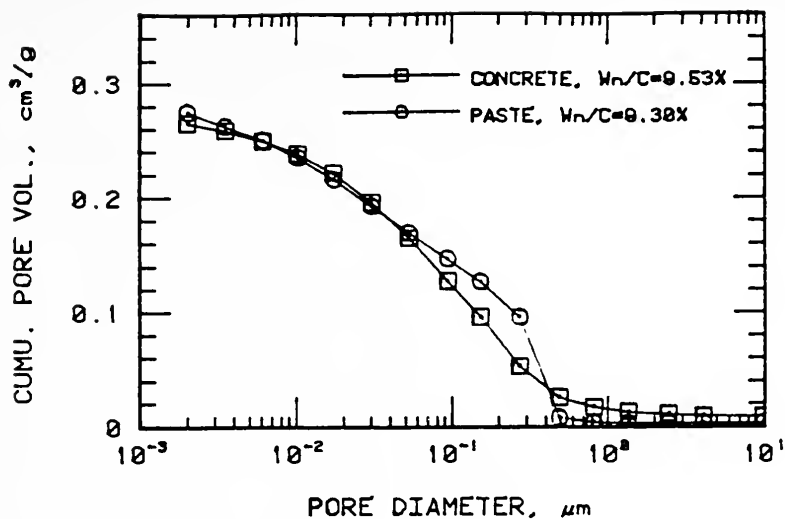paste in concrete and mortar with w/c=0.55 at an early age.

Fig.4 The pore size distributions of the paste and the paste
in concrete and mortar with w/c=0.55 at a later age.

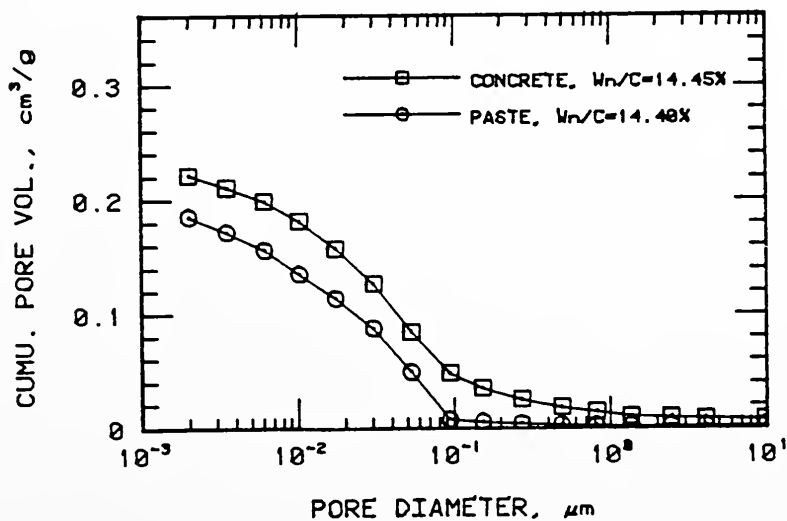Fig.5 The pore size distributions of the paste and the paste in concrete hydrated at $10^{\circ}C$ at an early age.

Fig.6 The pore size distributions of the paste and the paste in concrete hydrated at $10^{\circ}C$ at a later age.
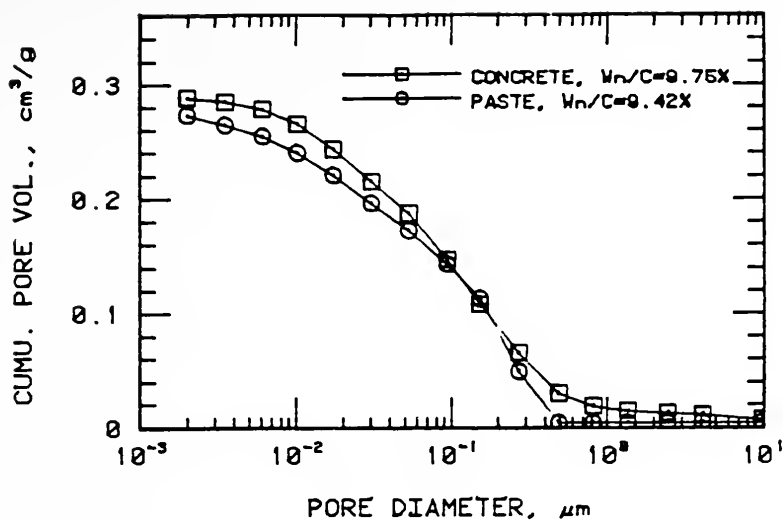
Fig.7 The pore size distributions of the paste and the paste in concrete hydrated at 30°C at an early age.
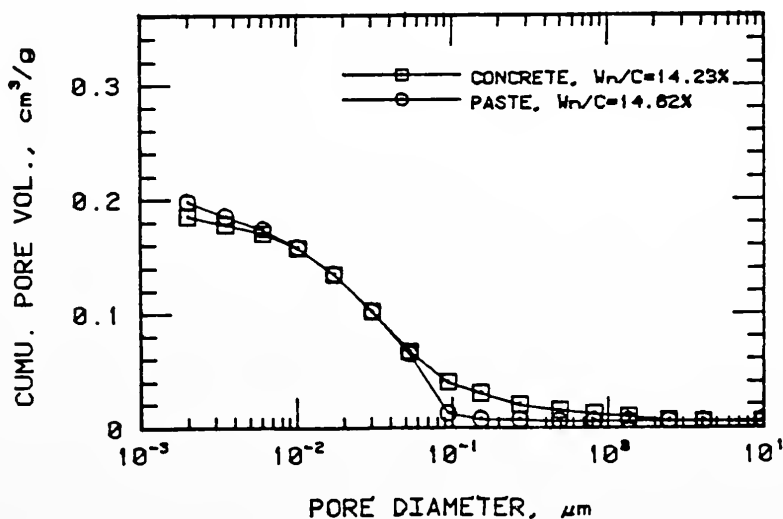

Fig.8 The pore size distributions of the paste and the paste in concrete hydrated at 30°C at a later age.
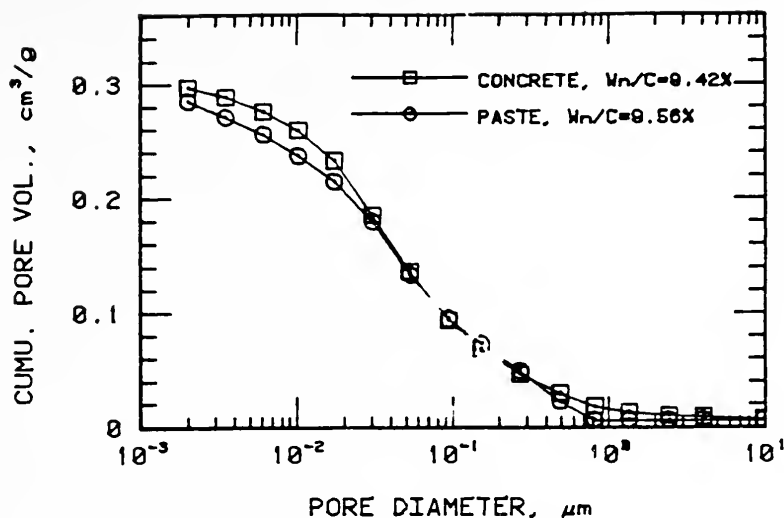
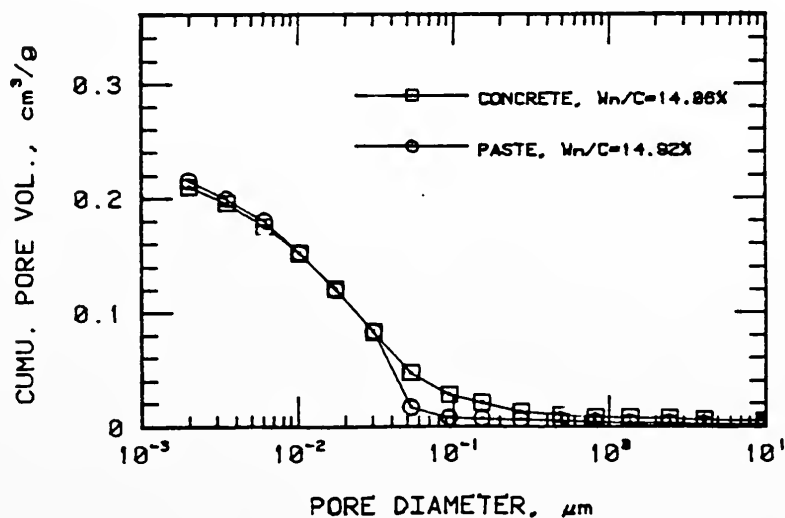Fig.9 The pore size distributions of the paste and the paste in concrete with 2% $CaCl_2.2H_2O$ at an early age.

Fig.10 The pore size distributions of the paste and the paste in concrete with 2% $CaCl_2.2H_2O$ at a later age.
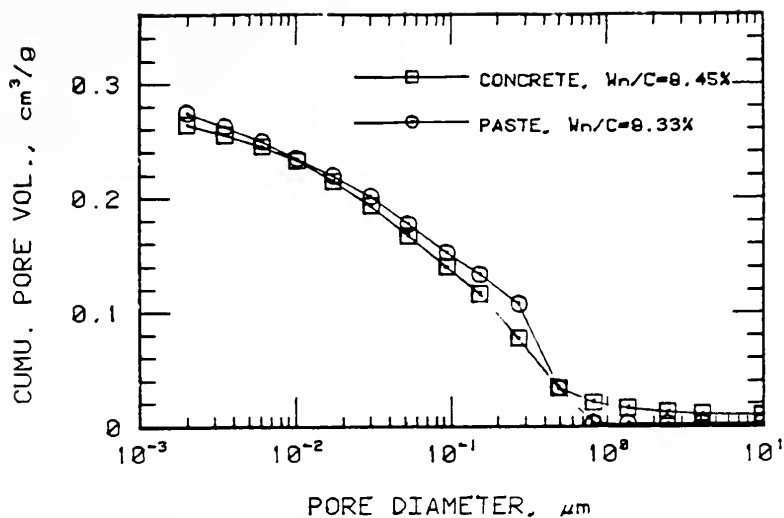
Fig.11 The pore size distributions of the paste and the paste in concrete with 0.15% citric acid at an early age.
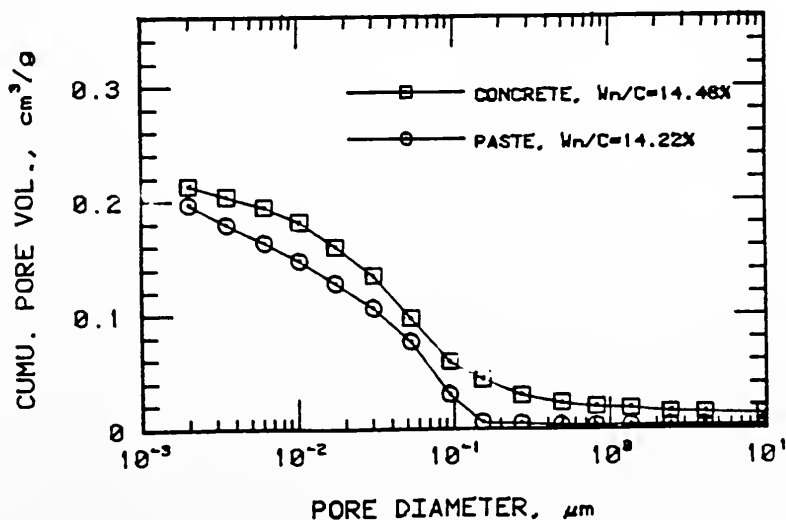

Fig.12 The pore size distributions of the paste and the paste in concrete with 0.15% citric acid at a later age.

Fig.13 The pore size distributions of the pastes in con-
crete with w/c=0.45 and concrete of Class A at an early age.

Fig.14 The pore size distributions of the pastes in concrete
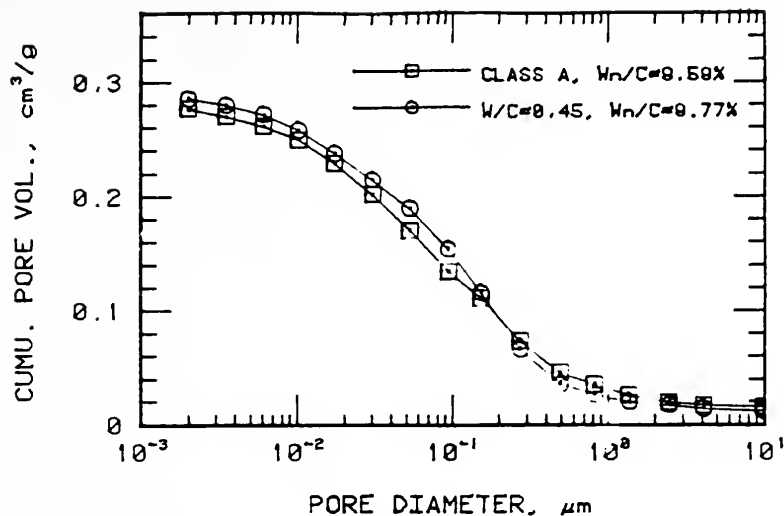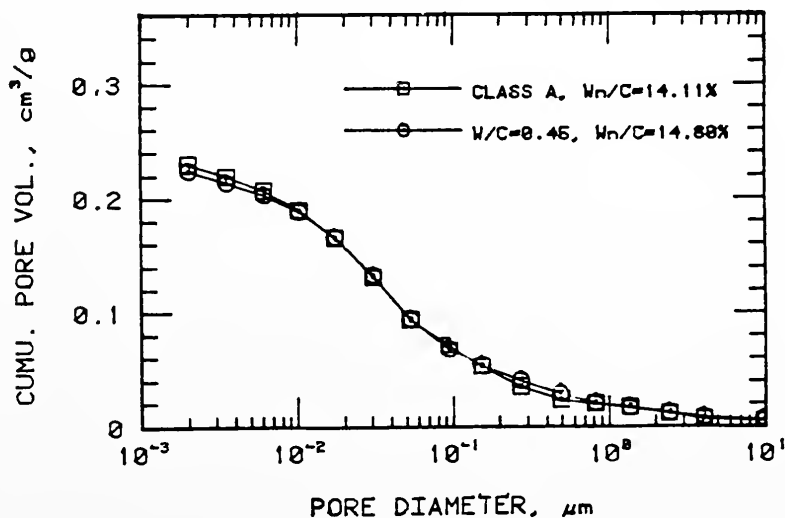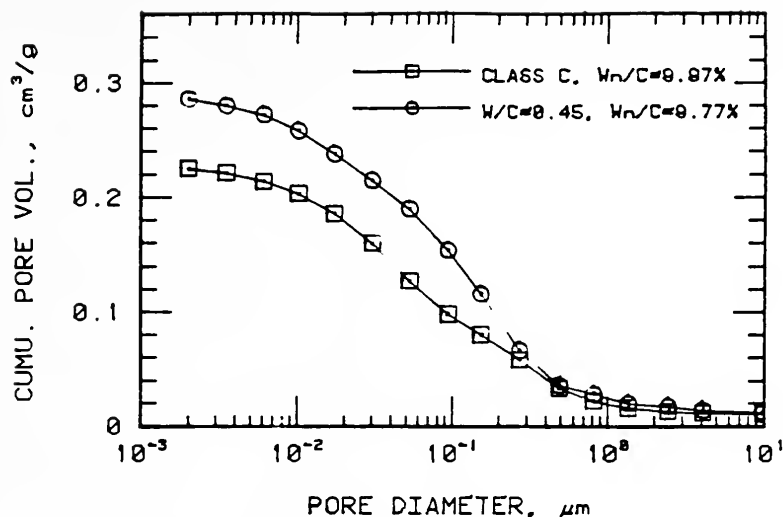with w/c=0.45 and concrete of Class A at a later age.

Fig.15 The pore size distributions of the pastes in concrete with w/c=0.45 and concrete of Class C at an early age.
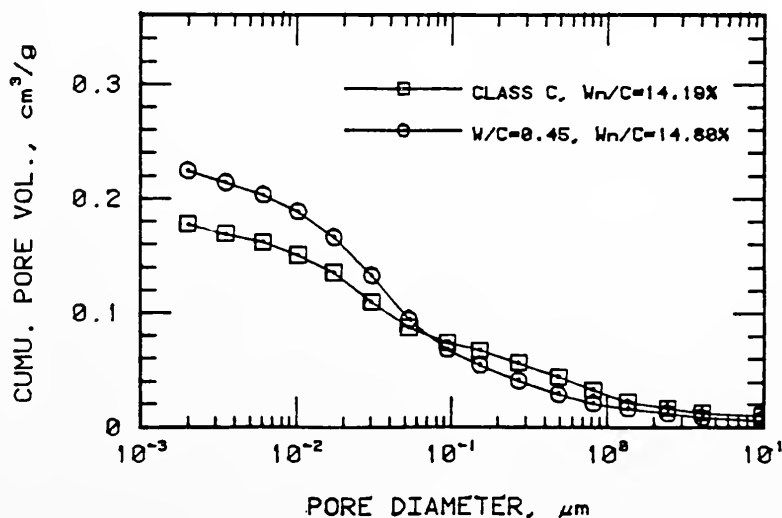

Fig.16 The pore size distributions of the pastes in concrete with w/c=0.45 and concrete of Class C at a later age.

DISCUSSION

In this study, the pore structures of plain pastes were measured along with those of similar pastes formed in concrete. Furthermore, the measurements were made on pastes that had hydrated, although under different circumstances, to the same degree of hydration (i.e. equal amounts of reaction). This is an unusual feature of this work. Most studies compare samples at the same ages, not at the same degree of reaction. The main objective of the study was to measure to pore structure of paste in concrete. However, since the study also provided an unusual opportunity to investigate plain pastes, these will be discussed first.

The Pore Structure of Cement Paste

The pore size distributions of differently hydrated cement pastes were measured at two degrees of hydration, non-evaporable water contents of about 9.5% and about 14.5%. At different degrees of hydration, the pore size distributions would be expected to be different, even for the same kind of paste. Since the comparisons here are based on the same degrees of hydration, it is assumed that any observed

differences are due to differences in the nature of the hydration products that have formed under differing hydration conditions.

At the same degree of hydration and water:cement ratio, the pore size distributions of all the pastes are nearly the same with the exception of the paste containing CaCl. This paste has a reduced volume of the larger pore sizes. The vigorous mixing in the presence of this accelerator caused some hydration during the mixing process and these pastes were noticeably thicker than the others when removed from the mixing chamber. Thus, these pastes were cast, and began to develop their permanent microstructure, at a more advanced state of hydration. It is believed that this produced an artificial difference in these pastes, and that they cannot be compared with the others.

If the calcium chloride containing pastes are left out, all the rest, with the same w/c and degree of hydration, have essentially the same pore size distributions. There is a potential scatter in the measurement of the intruded pore volume from sample to sample of about 0.01 cc/g. When this is taken into account, there appear to be no differences in the pore structure of pastes that hydrated under considerably different conditions. For example, accelerating hydration by heating to 30° C produces the same pore structure as retarding hydration by cooling to 10° C, if one waits for the retarded paste to react to the same extent.

When samples of different water:cement ratios, but hav-
ing the same degree of hydration, are compared, the larger
water:cement ratio pastes have the greater pore volume. The
differences between the pore size distributions of cement
pastes with water:cement ratios 0.45 and 0.55 are plotted in
Fig.17 for both degrees of hydration. At an early stage of
hydration, it can be seen that the difference in the cumula-
tive pore volumes occurs virtually all in the pore diameter
range bigger than about 0.3 μm. The additional water has
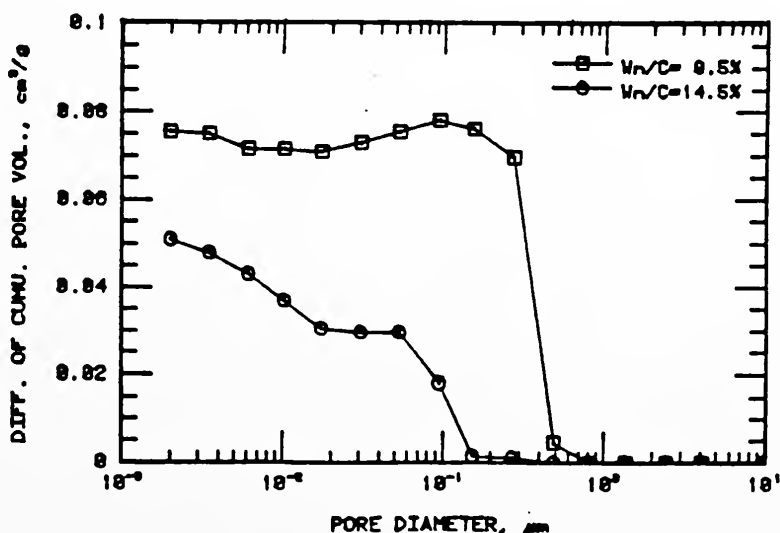apparently been used to make only the larger pores.

Fig.17 The differences between the pore size distributions
of cement pastes with w/c 0.45 and 0.55.

However, at a greater degree of hydration, differences are found across the entire range of pore sizes. Apparently further hydration has subdivided the larger initial pores into smaller ones of all sizes.

All the pore size distributions presented so far have had the pore volume displayed on a per unit mass of dry paste basis. One can also display pore volume as a percent of the total intruded volume. Figures 18 and 19 show the results of doing this for the two degrees of hydration of the pastes with the two different water:cement ratios. The less mature and higher water:cement paste of Figure 18 has a somewhat greater percentage of larger pores. However, the more mature pastes of Figure 19 have virtually the same percentages of all sizes of pores. This is the same point that was made in Figure 17, but presented in a different way. The additional pore space generated by the additional water is distributed uniformly across the pore sizes in mature pastes.
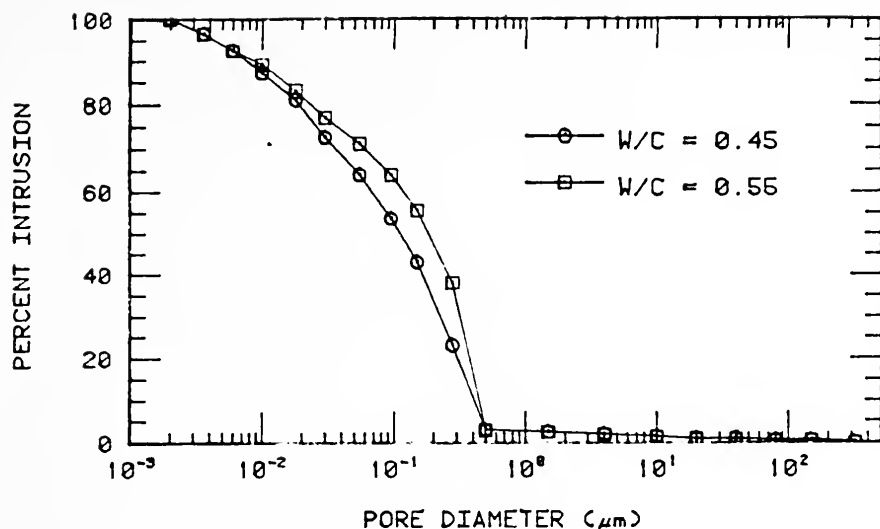
Fig.18 The percentage pore size distributions of cement
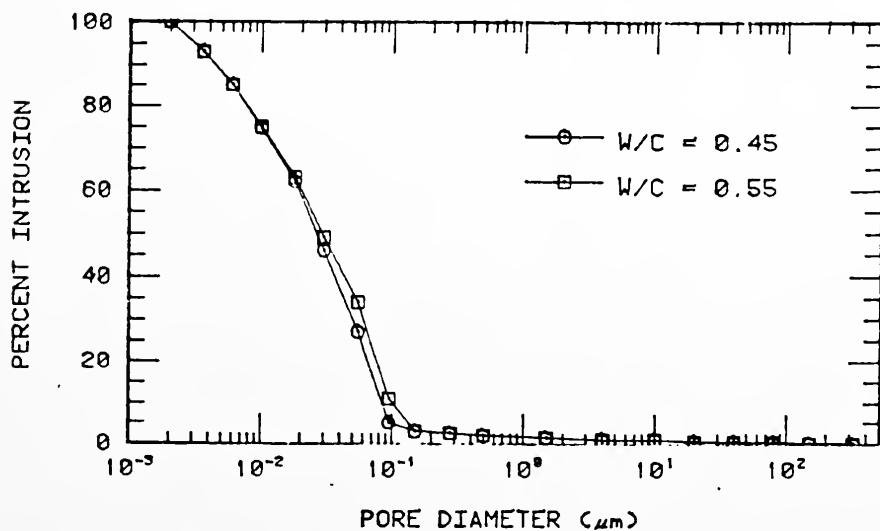pastes with w/c 0.45 and 0.55 for young pastes

Fig.19 The percentage pore size distributions of cement
pastes with w/c 0.45 and 0.55 for mature pastes

The Pore Structure of the Paste in Mortar and Concrete

In engineering practice the pore structure of concrete is of major concern, because it influences properties such as permeability and durability. The presence of aggregate has, in the past, precluded the determination of the pore structure of the paste in concrete. The present research represents the first direct determination of this pore structure that is free from the interfering factor of the porosity of the aggregate.

From Fig.1 to Fig.12 it can be seen that the pore size distributions of the paste in mortar and concrete have the same general shape as those of plain pastes. However, the paste in concrete is more porous than a corresponding plain paste. Much of the additional pore volume occurs in pores with diameters greater than the threshold diameter of the plain paste. This finding shows that the presence of the aggregate does, indeed, influence the microstructure of the paste that forms around it. Generally, this influence is more pronounced in the case of more mature concretes, as compared with those of lesser maturity.

This is the essential finding of this study. There are two important aspects to this finding. One is that the bulk of the additional pore volume in concrete paste lies in the

largest pore size range. These are the pores that are most likely to affect adversely properties such as permeability and durability.

The other important aspect is that the pore structure of plain paste is not a good model for the porosity of the paste as it exists in concrete. In the past it has been assumed that plain pastes and concrete pastes had the same pore structure. Correlations based on this assumption are inevitably biased and perhaps fatally flawed.

The results of this study show that the paste that develops in a mortar has essentially the same pore structure as that in a concrete. This finding is not unexpected, because the fine aggregate, possessing the majority of the surface area of the total aggregate, would be the major factor in any alteration of the paste. A practical consequence of this is that the pore structure of the paste in a mortar is a good model for concrete, and is much easier to study.

One can examine the differences caused by the aggregate by plotting the cumulative difference in intruded pore volume vs. pore diameter. A typical result is given in Figure 20, for both levels of hydration. Plots for the other pastes and concretes in this study have a similar appearance. One can see that, in the pore size range larger than the threshold diameter, the paste in concrete has a bigger intrusion volume and the difference increases to a maximum
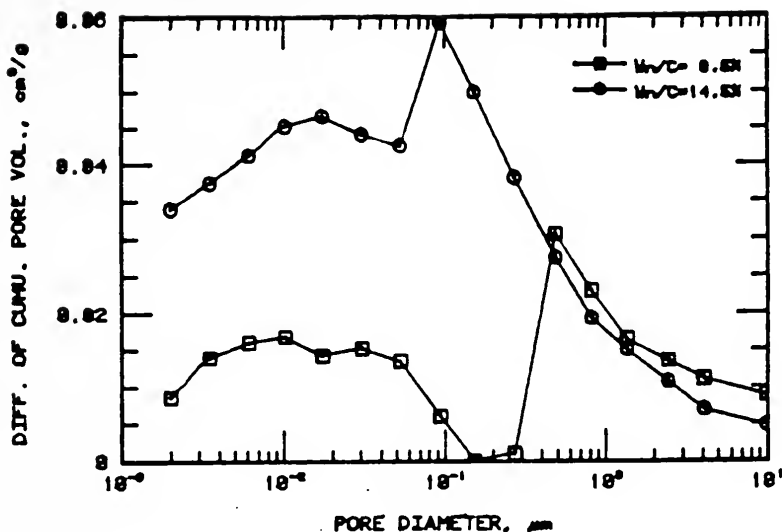
Fig.20   The differences of pore size distributions of the paste in concrete and the plain paste with w/c=0.45.

at the threshold diameter. In the pore size range just smaller than the threshold diameter, the plain paste apparently has more pore volume than the paste in the concrete. (The curves in Figure 20, and all the others as well, drop.) However, the plain pastes never catch up to the concretes which always have a greater total pore volume.

When the threshold diameter decreases with additional hydration, the maximum difference, in curves such as Fig.20, moves with it along the diameter axis. This result shows that the additional pore volume is intimately associated with the hydration process. So, whatever the maximum pore

size of a plain paste may be, the corresponding paste in a concrete always has a significant pore volume with slightly larger diameters.

One possible explanation of this phenomenon is that plain pastes do, in fact, have pores larger than their threshold diameter. However, these pores are not intruded by mercury until it can pass through narrower entrance pores having the threshold diameter. The presence of the aggregate may be disrupting the paste in such a way that it has larger entrances that allow the larger interior pores to be intruded at the appropriate pressure rather than at an artificially higher one.

At a later stage of hydration, a bigger difference is seen between the total intruded volumes of the plain paste and the paste in concrete. Of course, the total pore volumes of both are reduced as hydration proceeds. However, the difference between the two widens. This seems to indicate that, as more hydration product is produced, the disruptive effect of the aggregate becomes more pronounced, and more disrupted paste is present.

If one compares the pore structures of the pastes in concretes hydrated under different circumstances one finds the same result that was found for the plain pastes. When the water:cement ratio and degree of hydration are the same, the pastes have the same pore size distributions regardless

of the circumstances of their hydration.

Since it has been well documented that any acceleration of early hydration results in a lower ultimate strength, and vise-versa for early retardation, the above finding supports the idea that the strength difference is caused by some "quality" difference in the solid hydrate, since the influence of pore structure on strength has been eliminated from the comparison.

The Pore Structures of Class A and C Concretes

The pore structures of two concretes that have been extensively used by the Indiana Department of Highway were also studied. As shown in Fig.13 and Fig.14, Class A concrete has nearly the same pore size distributions as the control concrete used in this study. As shown in Fig.15, Class C concrete has a smaller pore volume than the control concrete. This is due to the smaller water:cement ratio of the former. The distribution curves are seen to have the same general shape as those of the other concretes that were examined. Thus, the conclusions obtained in this study would seem to be applicable to these concretes that are used in actual practice.

CONCLUSIONS

The characteristics of the pore size distribution of the paste in concrete and mortar can be summarized in the following points.

1. The cement paste that forms in concrete has a pore structure that is different from that in plain paste.

2. The paste in concrete is more porous, and the majority of the extra porosity has larger diameters than are found in plain paste.

3. The paste that forms in mortar has essentially the same pore structure as that in concrete.

4. Pastes with the same w/c that hydrate under different circumstances, but to the same degree of hydration, have the same pore size distributions.

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APPENDIX

Determination of the Cement Content in Concrete and Mortar

The sample is assumed to contain about 1 to 2 grams of cement.

1. Place sample in a 250 ml beaker. Add 25 ml of concentrated HCl and 75 ml of water, and leave the sample to digest. Usually it takes 1 day for an ignited concrete sample and 2 days for a mercury intruded sample to be completely decomposed.

2. When the sample is completely decomposed, wash the solution by decantation into a 1 liter volumetric flask. Use five portions of about 150 ml each. Make the contents of the volumetric flask up to volume.

3. Take 10 ml of the solution from the volumetric flask, and determine the content of CaO by EDTA titration as follows:

    1. Reagents:

        1. Standard Calcium Solution, 0.01 M. Weigh 2.000 g of dried primary standard-grade $CaCO_3$, and dissolve in 100 ml HCl(1:19).

Boil to expel carbon dioxide, cool, and dilute to exactly 2 liters. One milliliter of this solution is equivalent to 0.0005608 g CaO.

2. EDTA Solution 0.01 M. Dissolve in water 3.73 g of the disodium salt of EDTA per liter of final solution. Standardize using 50 ml of standard calcium solution.

3. Buffer, pH 12.5 (KOH Solution). Dissolve 185 g of KOH/liter of water, and store in a polyethylene bottle.

4. Hydroxy Naphthol Blue Indicator.

5. Triethanolamine (1:4).

6. Hydroxylamine Hydrochloride Solution (10 percent, w/v).

2. Procedure: Pipet a 10-ml aliquot of the sample solution into a 400-ml beaker; dilute with water to about 150 ml. While stirring, add in the following order: 5 ml hydroxylamine hydrochloride, 10 ml triethanolamine, and 0.01 M EDTA solution equivalent to about 95% of the calcium present. Raise the pH to 12.5 by adding 20 ml of KOH buffer, and stir for about 2 minutes. Add about 0.2 to 0.3 g of hydroxy naphthol blue indicator,

and titrate with 0.01 M EDTA solution until the color changes from wine red to blue.

3. Calculation:

$$\text{weight of CaO} = \frac{V1 \times F1 \times 1000}{A}$$

where:

        V1 = volume of EDTA for titration (in ml)

        F1 = grams CaO/ml EDTA (1 ml 0.01 M EDTA = 0.0005608 g CaO)

        A = volume of aliquot (in ml)

4. The mass of cement is calculated from the mass of CaO by knowing the CaO content of the original cement. This is determined by using the above method on the unhydrated cement.

5. The mass of paste is calculated from the mass of cement and the non-evaporable water content.